TITLE: **Improved Catalyst for Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nonporous Host**

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1. OBJECTIVES

The focus of this project is to improve the catalytic performance of zeolite Y for petroleum hydrocracking by synthesizing nanoparticles of the zeolite (~20-25 nm) inside high surface area, highly ordered nanoporous silicate or aluminosilicate hosts, such as SBA-15. The encapsulated zeolite nanoparticles will have reduced diffusional path length, hence hydrocarbon substrates will diffuse in, are converted and the products quickly diffused out. This prevents over-reaction from occurring and the blocking of the zeolite pores and active sites are minimized. The nanoporous hosts also serves to: a) perform as a mild hydyrocracking catalyst in their own right, to do the initial breaking down of bulky heavy oil substrates and b) screen bulky hydrocarbon substrates from blocking the entrance to the zeolite pores, and reduce the extent of non selective, undesirable reactions on the external surfaces of the zeolite nanocrystals. The project consists the following main tasks: a) synthesis of the 30 nm pore diameter nanoporous materials. This will be done using poly (alkylene oxide) copolymers as template around which inorganic precursors are organized. Subsequently removal of the copolymer will yield a nanoporous material, the pore sizes of which will depend on the number of poly (alkylene oxide) units; b) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) within the pores of the nanohosts using various techniques such subjecting a conventional zeolite Y synthesis mixture to temperatures below <5°C, high speed and/or, ultrasonic agitation and crystal growth suppression controlled by the pore size of the nanohosts; c) Testing the nano-composite catalysts for the catalytic conversion of heavy petroleum substrates.

2. ACCOMPLISHMENTS TO DATE

Zeolite Y nanoparticles were synthesized in the presence of tetramethylammonium ion. The filtered clear solution containing tetramethylammonium (TMA), tetraethylorthosilcate (TEOS), aluminum powder, and sodium chloride with molar composition $3.4TEOS:0.83Al_2O_3:4.6TMA:0.1NaCl:300H_2O$ was aged at room temperature for 4 days and then crystallized at 100C for 11-18 days. In the absence of TMA the average particle size was 284 nm, whereas a TMAOH yielded zeolite Y nanocrystals with average particle size of 97 nm as measured by both dynamic light scattering and atomic force microscopy.

In our attempt to prepare nanoporous host, ordered high surface mesoporous phenylene-bridged organosilicate was synthesized from the base catalyzed hydrolysis and condensation of 1,4-bis(triethoxysilyl) benzene (BTEB) precursor in the presence of a cationic surfactant, $(CH_3(CH_2)_{15}N(CH_3)_3Cl$, as template. The product has a high degree of structural ordering, and a crystal- like pore wall with a spacing of 7.6 Å along the channel direction. The material possessed well defined pores averaging 31 Å, a pore volume of 0.58 cm^3/g, and BET surface area of 876 m^2/g. Approximately 80 % condensation of the organosilicate precursor was observed and the Si-C bonds remained intact during the process. The organic template can be effectively solvent extracted and the organosilicate pore walls are thermally stable up to 550ºC in air. In addition, the acid catalyzed hydrolysis and condensation of 1,4-bis(triethoxysilyl) benzene (BTEB) precursor in the presence of a nonionic oligomeric surfactant, $CH_3(CH_2)_{17}(OCH_2CH_2)_{10}OH$, (Brij 76) as template, yielded an ordered high surface mesoporous phenylene-

bridged organosilicate with well defined pores averaging 27.4 Å, a pore volume of 0.46 cm3/g, and BET surface area of 784 m^2/g. The organic template can be solvent extracted and the organosilicate pore wall is thermally stable up to 550ºC in air.

3. FUTURE WORK

The work planned for the remaining project period of this program include the following tasks:

- Continue to investigate methods to reduce the particle sizes of zeolite Y nanocrystals to about 30 nm, such as using tetramenthylammonium bromide in synthesis mixtures as crystal growth suppressor.
- Continue to investigate methods to synthesize stable highly ordered nanoporous silicate hosts with expanded pore size up to 30 nm. Methods explored to date (such as the use of pore size expanders e.g. trimethylbenzene) have given poor results.
- Encapsulate zeolite Y nanoparticles in the nanoporous hosts.
- Investigate the catalytic performance of zeolite Y encapsulated in nanoporous hosts for heavy oil petroleum feedstock conversion.
- Publish the outcome of these investigations.

4. LIST OF PAPERS PUBLISHED, CONFERENCE PRESENTATIONS AND STUDENTS SUPPORTED UNDER THE GRANT

Publications and presentations

- Non Ionic Surfactant Mediated Templated Synthesis of Phenylene-Bridged Organosilicate, Yohannes Ghirmazion*, Conrad Ingram, presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.
- A Comparison of Synthesis Strategies for Aryl Functionalized Ordered Nanoporous Organosilicates using Nononionic and Cationic Surfactants, Yohannes Ghirmazion*, Conrad Ingram presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.
- On the Synthesis of Zeolite Y Nanocrystals in the Presence of Tetramethylammonium Bromide, Yohannes Ghirmazion* and Conrad W. Ingram, presentated at the 227 ACS National Meeting, Anaheim, California, March 28 - April 1, 2004 .
- Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis, Conrad Ingram* and Yohannes Ghirmazion, accepted for presentation at the 4th International Mesostructured Material Symposium, May 1st -4, 2004, Cape Tow, South Africa.
- Synthesis of Aromatic Bridged Ordered Mesoporous Organosilicate with Cetyltrimethylammonium Cation as Templating Agent has been accepted for a poster presentation at the 4th International Mesostructured Material Symposium, May 1st -4, 2004, Cape Tow, South Africa.
- Catalytic and selective behavior of MeAPO36 in the mild hydrocracking of heavy gas oil", Kesete Ghebreyessus and Conrad Ingram presented at the 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004.

Names of Students Receiving Support

Yohannes Ghirmazion	First year graduate student (Chemistry)
Taurean Hodges	Senior (Chemistry)
Ifedapo Adeniyi	Sophomore undergraduate (Chemistry & Engineering)